

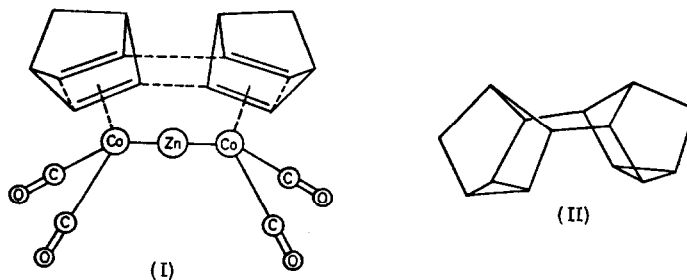
NEW CATALYSTS OF STEREOSPECIFIC NORBORNADIENE DIMERIZATION
TO "BINOR-S" (1,2,4:5,6,8-DIMETHENO-S-INDACENE).

G. N. Schrauzer, R. K. Y. Ho and G. Schlesinger

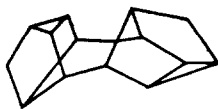
Department of Chemistry, The University of California, San Diego
Revelle College, La Jolla 92037

(Received in USA 18 December 1969; received in UK for publication 13 January 1970)

The "head-to-head" dimer of norbornadiene (bicyclo(2,2,1)heptadiene-2,5), "Binor-S" (1,2,4:5,6,8-dimetheno-s-indacene)(II)^(1,2) is formed in quantitative yield on dimerising norbornadiene with bifunctional transition metal catalysts such as $Zn[Co(CO)_4]_2$, with or without $BF_3 \cdot O(C_2H_5)_2$ or other Lewis acid cocatalysts, or with catalyst systems such as $Co_2(CO)_8/BF_3 \cdot O(C_2H_5)_2$ or $In[Co(CO)_4]_3/BF_3 \cdot O(C_2H_5)_2$. The extraordinary selectivity of the binuclear catalysts in promoting the formation of I has led to the postulate of transition states such as I leading to the product II via a π -complex multicenter process:



The assumed mechanism of formation is in accord with initial kinetic data on the reaction with $Zn[Co(CO)_4]_2/BF_3 \cdot O(C_2H_5)_2$ as the catalyst (e.g. the established dependence of the rates of reaction on the amount of catalyst and the square of the concentration of norbornadiene) and the fact that the hydrocarbon has the expected "syn" configuration.



III

The only other structural alternative would be the "anti" structure III, which is definitely eliminated by detailed IR and Raman spectrographic analysis^(3,4,5). In the present paper we wish to report several new catalysts which are nearly as effective but more readily accessible than those given above. They include $\text{CoBr}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$, $\text{CoI}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$, $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$, all with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ as the cocatalyst. The complexes are airstable and easily obtained from commercially available starting materials. The salts $\text{CoX}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$, for example, may be prepared from the anhydrous cobalt(II) halides and triphenylphosphine on refluxing in benzene. The catalysts are inactive as such, as evidenced in all cases by the induction period prior to reaction, during which time the original color of the solution changes to brown. Evidently, the metal complexes are reduced to the zerovalent state during the induction period, indicating that the catalytically active fragments may be metal-metal bonded species $(\text{Lig.})_n\text{M}-\text{M}(\text{Lig.})_n$ ($\text{M} = \text{Co}$ or Rh). The inability of $\text{CoCl}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$ to catalyze Binor-S formation under similar conditions is accordingly attributed to the greater polarity and stability of the complex salt. The reducing agent causing the conversion of the cobalt salts to the catalytically active species is presumably norbornadiene in conjunction with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. The catalysts are inactive in the absence of Lewis acids, or in dilute solutions of norbornadiene. The reactions were therefore run in pure norbornadiene⁽⁶⁾. In typical reaction runs, 20 ml of freshly distilled norbornadiene was placed into a flask equipped with reflux condenser. Catalyst (0.2 g of complex followed by 1 ml of freshly distilled $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$) was added and the dimerization initiated by gentle heating. As soon as the exothermic reaction begins⁽⁶⁾ the external heating must be removed. Occasional cooling is required to moderate the reaction. The reaction mixture is dissolved in methylene chloride, washed with dilute aqueous bicarbonate, filtered and

diluted with 100 ml of methanol. The methylene chloride is evaporated by gentle heating on a steam bath. The product, Binor-S, separates as a faintly yellow layer which crystallized on standing, m.p. 59-60°. Further purification to yield a product with the literature m.p. of 65-65.6°⁽¹⁾ is achieved through vacuum distillation, bp 73° (1-2 mm). The yields are essentially quantitative, other norbornadiene dimers are formed in amounts <1%. Binor-S thus is the most readily obtainable norbornadiene dimer. With conventional catalysts (e.g. $\text{Ni}(\text{CO})_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$) only mixtures of dimers other than Binor-S are obtained which are difficult to separate. $\text{Ir}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2$, in conjunction with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ also promotes Binor-S formation, although the yields achieved thus far are <10%. The important conclusion is that Binor-S is apparently formed only with cobalt, rhodium and iridium catalysts, hence with systems capable of producing catalytically active dimeric metal-metal bonded fragments. The nickel complex salts $\text{NiX}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$ (X = Cl, Br, I, CN), under identical reaction conditions produce glassy norbornadiene polymers and no trace of Binor-S.

REFERENCES

- (1) G. N. Schrauzer, B. N. Bastian and G. A. Fosselius, J. Am. Chem. Soc. **86**, 4890 (1966).
- (2) G. N. Schrauzer, Advances in Catalysis, Vol. 18, Academic Press Inc., New York, (1968), pp. 373-396.
- (3) Performed by A. C. Jones, Shell Development Company, Emeryville.
- (4) Katz and Acton⁽⁵⁾ expressed doubts in our previous structural assignment of Binor-S and felt that it could have the "anti" structure III. Their only support for this claim was the apparent absence of some IR bands (e.g. at 2914, 1045.5, 840.2 and 798.8 cm^{-1}) in the Raman spectrum. However, the four bands listed are weak and all close to intense Raman absorptions. Using high resolution Raman spectroscopic techniques (e.g. laser beam excitation and extinction of intense bands by polarization) the four bands are observable. The presence of a center of inversion in Binor-S is definitely eliminated by the essentially complete coincidence of the observable IR and Raman frequencies, and the total number of vibrational bands observed. A detailed report of the IR and Raman data is in preparation.
- (5) T. J. Katz and N. Acton, Tetrahedron Letters **1967**, 2601
- (6) Warning! Binor-S syntheses occasionally may proceed with explosive violence. Adequate safety precautions (good ventilation of laboratory, absence of open flames and use of efficient cooling baths such as acetone/dry ice) are recommended.